THE EFFECT OF SOLVENT PRETREATMENT ON COAL LIQUEFACTION

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This paper describes research on the chemical and physical phenomena occurring between coal and solvents prior to the onset of the major liquefaction (bond breaking) step. This report is limited to those phenomena that occur readily at temperatures near 200°C and have an effect on the subsequent liquefaction reactions.

A series of microautoclave experiments with Bruceton Coal and W. Kentucky 9/14 Coal, using creosote oil or SRC-II heavy distillate as solvents, showed that small but experimentally significant increases in conversion can be obtained by heating the coal-solvent slurry for one hour at 200°C prior to a short contact time liquefaction test (Table 1). (The presence of hydrogen at 200°C did not appear to be essential for this increase to occur.)

In order to obtain a better understanding of the factors that cause this increase in conversion, and thus propose a means to enhance the effect, several experiments were conducted with coal and model solvent compounds. Quinoline, 1-methylnaphthalene, and blends of these two compounds were chosen as solvent models. The results of these experiments show that these compounds are incorporated into the coal with pretreatment at 200°C, but no incorporation occurs with similar pretreatment at room temperature.

A tetrahydrofuran (THF) soluble-cyclohexane insoluble fraction was isolated from the quinoline treated coal and purified by three successive dissolution and reprecipitation steps in THF and cyclohexane. Nitrogen analysis of the products showed that the original value of 3.3 percent was reduced to 1.9 percent after three reprecipitation steps. Further reprecipitation resulted in no further decrease in the amount of nitrogen present. Comparing these values with the 1.5 percent nitrogen in the original coal shows two-thirds of the original quinoline incorporated into the coal was removed by the dissolution/precipitation steps. This fraction of the initially retained quinoline is considered to be physically incorporated into the pore structure of the crude quinoline-coal adduct. This quinoline is not readily removed by extraction but is removable by dissolution followed by reprecipitation in excess cyclohexane.

The quinoline remaining in the thrice-reprecipitated product is believed to be bound by hydrogen bonds to acidic sites, presumably phenolic. A comparison of the microautoclave liquefaction behavior of this adduct with a corresponding fraction of the coal obtained by analogous treatment of the coal with 1-methylnaphthalene did not show any significant difference. Inasmuch as the 1-

methylnaphthalene treatment of coal at 200°C could not result in acid-base adduct formation it was concluded that the coal quinoline adduct has no significant effect on subsequent liquefaction.

The possibility of a beneficial effect of the physically incorporated solvent was considered. Physical incorporation of the 1-methylnaphthalene as well as quinoline and blends of these compounds occurs readily at 200°C. These physically incorporated solvents are not removable by extraction, apparently because they enter the fine pore structure of the coal when the coal swells and are then locked into the pores when cooling of the coal solvent slurry causes the pore structure to shrink to near its original dimensions.

The beneficial effect of the solvent pretreatment is therefore believed to be a result of a greater extent of solvent aided liquefaction in contrast to the pyrolytic decomposition of some of the coal that reaches liquefaction temperatures before it is contacted by solvent.

Table 1. Effect of Solvent Pretreatment

(1g coal, 5g solvent, 2000 psig, 425°C)

Coal	Solvent	Pretreatment		Run Time	THF Solubles (%)
		Time	Temperature		
Bruceton	Creosote Oil	None	--	15 min.	61.5
Bruceton	Creosote Oil	1 hour	200°C	15 min.	66.7
Bruceton	SRC-II, H.D.[a]	None	--	15 min.	75.6
Bruceton	SRC-II, H.D.	1 hour	200°C	15 min.	78.2
W. KY 9/14	SRC-II, H.D.	None	--	5 min.	85.7
W. KY 9/14	SRC-II, H.D.	1 hour	200°C	5 min.	88.1
W. KY 9/14	SRC-II, H.D.	15 min.	320°C	5 min.	88.2
W. KY 9/14	Creosote Oil	None	--	5 min.	79.5
W. KY 9/14	Creosote Oil	1 hour	200°C	5 min.	81.8

[a]H.D. = Heavy Distillate

ANALYSIS OF LIGNITE LIQUEFACTION PRODUCTS PROCESSED WITH SYNGAS AND HYDROGEN SULFIDE

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The Grand Forks Energy Technology Center has successfully processed low-rank coals in their continuous processing unit (CPU) in the bottoms recycle mode both with and without added H_2S. The addition of H_2S has been shown to enhance operability and to increase the yield and improve the quality of the distillable oils (1-3).

Products from four runs which compared the effect of added H_2S and different startup solvent were analyzed for H-donor content as a measure of recycle liquid quality and for incorporation of sulfur into organic compounds. The coal processed was a Beulah North Dakota lignite (B3).

The run conditions are shown in Table I and the coal analysis in Table II. Startup solvents included a hydrogenated anthracene oil distillate (HAODI), and surrogate recycle solvent (SS) formulated from an anthracene oil and SRC II middle distillate (4). Syngas was a 1:1 mole mixture of CO and H_2.

TABLE I

CONTINUOUS PROCESS UNIT-SLURRY RECYCLE TEST
RUN CONDITIONS

CPU Run No.	41	65	72	79
Start Up Solvent	HAOD1	SS	SS	SS
Coal	B3	B3	B3	B3
Gas	Syngas	H_2	Syngas	H_2
Temperature, °C	460	460	460	460
Pressure, psi	4000	2600	2600	2600
Added H_2S	No	No	Yes	No

TABLE II

ANALYSIS OF BEULAH NORTH DAKOTA LIGNITE (B3)

Proximate Analysis As-received		Ultimate Analysis Moisture-free	
Moisture	28.84	Ash	16.44
Volatile matter	28.99		
Fixed carbon	30.76	Moisture and ash-free	
Ash	11.70		
Heating value		Carbon	69.49
Btu/lb	6,731	Hydrogen	4.43
		Nitrogen	0.99
		Oxygen (diff)	22.26
		Sulfur	2.81

RESULTS AND DISCUSSSION

Separations of the light oils and recycle slurry ASTM D-1160 distillates were carried out by extraction and silica gel column chromatography as described previously (5). The extraction fractions included two phenolic fractions, a basic fraction and a hydrocarbon fraction. The hydrocarbon fractions were analyzed by quantitative ^{13}C NMR spectroscopy (6) and the phenols were determined by capillary gas chromatography on a 60m DB5 fused silica column (7). No significant differences in concentrations of phenols were noted, and no sulfur was detected in the phenolic fractions.

All of the extracted fractions were tested for mutagenicity (Ames test). The results showed no detectable response to the hydrocarbon and phenolic fractions from either Run 72 (with H_2S) or Run 79 (without H_2S). The activity of the basic fractions was within the expected response region usually associated with coal-derived liquids.

An additional separation of the light oils and recycle slurry ASTM D-1160 distillates was effected by silica gel column chromatography (5). The twelve fractions were analyzed by capillary GC (DB5 60m column) using a post-column splitter with a flame ionization detector (FID) and a flame photometric detector (FPD) specific for sulfur compounds. The concentration of the main sulfur-containing organic compound, dibenzothiophene was essentially the same for the D-1160 ASTM distillates for two of the runs (Runs 72 and 79) which were carried out with and without H_2S, 0.28 and 0.31% respectively. A typical chromatogram is shown in Figure 1. The presence of dibenzothiophene and two C_1-dibenzothiophene isomers was confirmed by capillary GC-MS analysis. The comparative analyses of the light oil column fractions from Runs 72 and 79, with and without H_2S, showed that the light oil from Run 72, to which H_2S was added contained a much larger variety of organic sulfur compounds and also contained elemental sulfur. Elemental sulfur elutes from the silica gel column with pentane in fractions 3 and 4 and gives an excellent response with the FPD but no response with the FID.

Analyses of the ASTM D-1160 distillate column fractions for H-donors indicated that the distillates obtained from Run 72 (H_2S added) yielded the same or higher levels of H-donors even though the partial pressure of hydrogen, P_{H_2}, was only about half that of Run 79 without H_2S. Since there is usually a strong dependence of H-donor concentrations on the P_{H_2}, (Table III), this result is apparently due to the presence of H_2S.

TABLE III

COMPARISON OF H-DONOR CONCENTRATIONS AT VARIOUS P_{H_2} WITH AND WITHOUT H_2S, 450°C, P_T = 2600 PSI, (% IN RECYCLE SLURRY ASTM D-1160 DISTILLATE). LIQUEFACTION OF BEULAH (B3) LIGNITE.

Run No.	65	79	72
H_2S	No	No	Yes
P_{H_2} (psi)	2582	1986	1199
H-Donors (%)			
Tetralin	0.85	0.17	0.10
6-Methyltetralin	0.65	0.10	0.64
Dihydrophenanthrene	0.41	0.25	0.40
Tetrahydrophenanthrene	0.19	0.09	0.28
Octahydrophenanthrene	0	0	0.06
Dihydropyrene	0.12	0.02	0.09
Tetrahydropyrene	not determined	0.20	0.34

The presence and variety of organic sulfur compounds present in the products depends on sulfur compounds present in the starting solvent during the first 12-14 passes. Two CPU runs with B3 coal started up with different solvents showed different amounts and varieties of organic sulfur compounds in their distillable oils. Run 40 started up with AOD1 (1.4%S) gave a much more complex FPD sulfur trace for many of the silica gel column fractions than fractions from CPU runs started up with SS (0.4%S). The pattern noted is reproduced in the coal liquids formed (Figure 2).

CONCLUSIONS

1. A method for monitoring the presence of elemental and organic sulfur compounds in distillable low-rank coal liquefaction products utilizing column chromatography and dual detection (FID/FPD) capillary GC has been developed.

2. The addition of H_2S to the continuous processing of Beulah, North Dakota lignite does not increase the amount or variety of sulfur-containing organic compounds in the recycle slurry ASTM-D1160 vacuum distillate products. It does, however, introduce sulfur and a variety of volatile sulfur-containing organics into the light oils condensed from the vapor phase in the reactor.

3. The presence and variety of sulfur compounds after 12-14 reactor passes reflects the introduction of these components in the startup solvent.

4. No increased mutagenicity was observed with the coal liquids processed with H_2S.

5. The production of H-donors in the recycle slurry ASTM D-1160 distillates was enhanced by the presence of H_2S.

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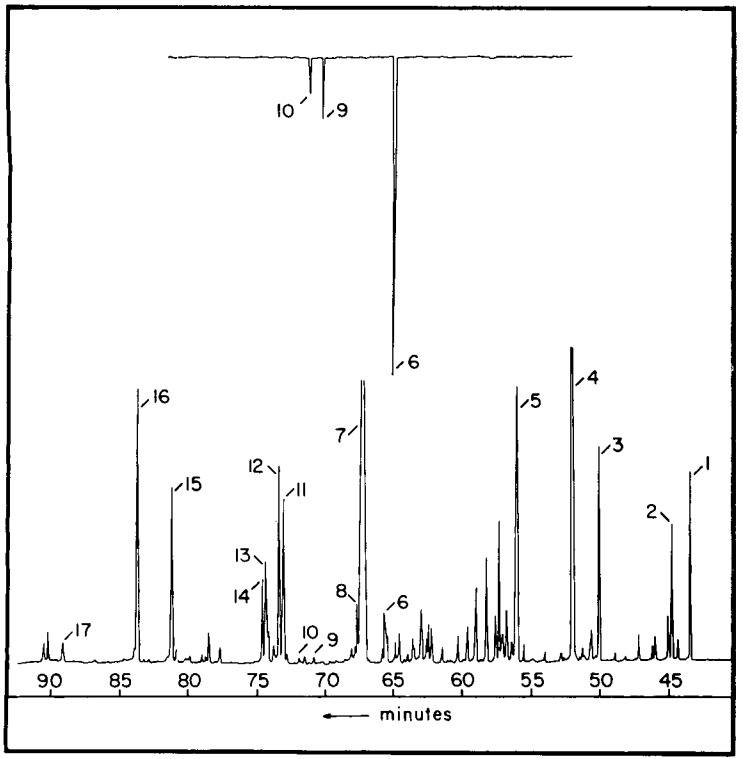

FIGURE 1. Capillary gas chromatography of light oil silica gel chromatographic fraction 7, Run 79, top trace sulfur detection by FPD, bottom trace, FID. 1. biphenyl, 2. 2-methylbiphenyl, 3. 3-methylbiphenyl, 4. dibenzofuran, 5. fluorene, 6. dibenzothiophene, 7. phenanthrene, 8. anthracene, 9. C, dibenzothiophene, 10. C, dibenzothiophene, 11. 3-methylphenanthrene, 12. 2-methylphenanthrene, 13. 4-methylphenanthrene, 14. 1-methylphenanthrene, 15. fluoranthene, 16. pyrene and 17. 2-methylpyrene

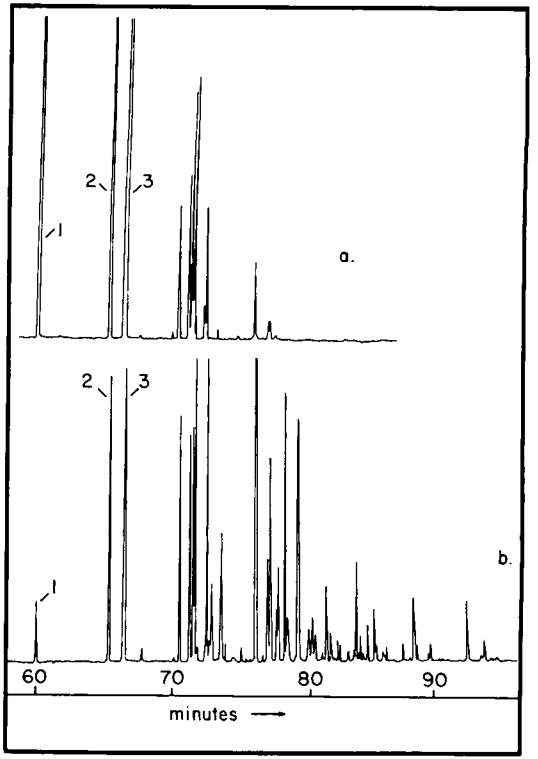

FIGURE 2. Capillary gas chromatography a). FPD trace of silica gel column fraction7 of light oil from Run 41 b). FPD trace of silica gel column fraction 7 of anthracene oil AOD1 startup solvent. (1. dibenzothiophene, 2. Cl-dibenzothiophene and 3. Cl-dibenzothiophene).

ANALYSIS OF THE n-HEPTANE SOLUBLE FRACTION OF COAL HYDROGENOLYSIS PRODUCTS BY HPLC

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Liquid products from the hydrogenolysis of coal are very complex and time and cost constraints limit the detail to which they can be characterized. Methods have been developed to separate the complex liquids into classes of chemical compounds and average properties of such fractions are often reported. Many of the separation schemes are adapted from methods applied to petroleum. Solvent extraction has been widely used to separate the liquid into hexane-soluble oils, asphaltenes and pre-asphaltenes (1). Liquid chromatography using ion exchange and clay columns has been used to separate coal liquids(2,3). Neutral oils were further fractionated on columns packed with silica and alumina to produce saturate, 1-ring aromatic, 2-ring aromatic and polynuclear aromatic fractions. Sequential elution by solvents allows separation into a larger number of fractions (4,5).

High performance liquid chromatography (HPLC) offers the potential for detailed yet rapid separation of complex liquid mixtures. Both solvent and column packing can be varied to give the desirable separation. In this research, the heptane soluble fractions from the heavy oil produced by hydrogenolysis of coals have been separated by HPLC and characterized by various analytical methods.

Experimental

The coal-derived liquid samples were obtained from the hydrogenolysis of coals in an entrained-flow reactor (6,7). The reaction was catalyzed with 6% $ZnCl_2$ at approximately 500° C and 12.4 MPa hydrogen pressure. The residence time varied from 20 seconds to 12 minutes depending on the properties of the coal. Seven samples from the study of Garr (6) were selected, as well as one medium volatile bituminous coal. Properties of the coals are listed in Table 1 (6,8). Coals were selected which showed a range of reactivity during hydrogenolysis. The yield of products and the properties of the heptane-soluble fraction are found in Table 2. Conversion is defined as one minus the toluene insoluble fraction. The heavy oil is defined as the material collected in the first condenser of the liquefaction reactor. It consists of the liquids transported in the vapor phase from the hot catch tank, boiling above approximately 100° C. The heavy liquid was extracted in Soxhlet apparatus to obtain the heptane soluble fraction.

The heptane soluble fraction was separated by two HPLC schemes. A Waters modular HPLC system was used with two solvent delivery systems, a solvent programmer, an automated sample injector, a UV absorbance detector, a differential refractometer detector, and a data module. The first scheme employed an NH_2 - μBondapak column. Saturates and non-polar aromatics were eluted with heptane at a flow rate of 2.0 ml/min. After 15 minutes, flow was reversed and a polar fraction was eluted. After 45 minutes, a 90/10 mixture of CH_2Cl_2/C_2H_5OH was introduced to elute a more polar fraction. This method is similar to that employed by Dark and McFadden (9). The second scheme employed a phenyl-μBondapak column and a non-linear gradient. The initial solvent was n-heptane. The gradient involved a 90/10 mixture of CH_2Cl_2/C_2H_5OH mixed with the heptane up to 75% over 36 minutes. A non-polar fraction was eluted by the heptane and a polar fraction was eluted by the gradient.

The heptane-soluble fractions were analyzed by carbon, hydrogen and nitrogen analysis and by vapor pressure osmometry (VPO). A Perkin-Elmer Model 240 CHN analyzer was used for elemental analysis. The VPO measurements were performed in dilute pyridine solutions.

The fractions collected by HPLC separations were analyzed by gas chromatography/ mass spectrometry. A 3% Dexsil 300 on Supelcoport was used for the separation. Approximately 300 mass spectral scans were recorded for each sample. Total ion chromatograms were obtained. Mass chromatograms were obtained for selected fragment masses. The fractions were also analyzed by Fourier Transform infrared techniques.

Results and Discussion

The conversion of the coal to toluene-soluble liquids, water and gases varies from 26% to 86%. The low conversion sample 7 is a lower rank coal and the conversion is mostly due to pyrolysis rather than hydrogenolysis. The residence time of this sample was only 20 seconds, indicating that the sample was blown through the reactor with little reactions. Samples which soften and agglomerate are retained in the reactor for longer times and show greater conversion. A sample with high conversion will pass through the reactor in 2-5 minutes while sample 6 required 12 minutes.

The molecular weight of the heptane-soluble fractions is about 285 and is independent of the degree of conversion or the properties of the starting coals. The hydrogen-to-carbon ratios vary from 1.08 to 1.41. The lower number corresponds to the medium volatile coal, which has a lower H/C ratio than the other coals. These values are averages for the entire fraction and do not indicate the range covered by the sample. More detailed analysis of a sample similar to No. 3 indicated a range of molecular weights of from 200 to 700 and the H/C ratio varied from 0.8 to 1.5 (10).

HPLC separation with the NH_2-μBondapak column produces a non-polar fraction that is eluted with heptane, a polar fraction that is adsorbed on the column and is eluted with heptane by reversing the direction of flow and a more strongly adsorbed fraction that is only removed by a polar solvent. Only the first fraction shows chromatographic separation. The elution pattern for each of the eight samples is very similar, differing only in the relative amounts of the three fractions.

HPLC separation with the phenyl-μBondapak column produces a non-polar fraction which elutes with heptane and a solar fraction that elutes with the increasingly polar solvent gradient. Samples 4, 6 and 8 showed considerable material eluting between the two fractions. The other samples showed only the two, rather distinct peaks. The phenyl-μBondapak column offers the potential for improved separations of the liquids.

The infrared spectra of all non-polar fractions are similar. They show moderate OH stretching near 3400 cm^{-1} and some C=O stretching at 1700 cm^{-1}. The aromatic C-H stretch is weak but there are bands due to aromatic species at 1600 cm^{-1} and 800 cm-1 and aliphatic compounds at 1455 cm^{-1}. The polar compounds show a stronger OH absorption and lower carbonyl intensities. The spectra of all polar fractions are similar.

The GC/MS results demonstrate that the non-polar fractions contain alkyl aromatics. The aromatic systems are highly substituted with alkyl chains and saturated rings. The polar groups contain phenols and diphenols in addition. These results agree with previous structural characterization of coal liquids (10, 11,12).

The HPLC separation offers the potential for separating and characterizing coal-derived liquids. However, the samples analyzed in this study did not show major differences, even though they were produced from different coals with different degrees of conversion.

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Table 1

Properties of Coals[a]

Sample No.	Coal, Field	Volatile matter, % mafb	H/C	Vitrinite reflectance, %	Inert macerals, %	Rank
1	Beehive, Wasatch Plateau	53.6	0.93	0.556	8.5	HVAB
2	Swisher, Wasatch Plateau	52.3	0.90	0.533	4.5	HVAB
3	Hiawatha, Wasatch Plateau	50.3	0.93	0.547	4.1	HVAB
4	Kaiser, Book Cliff	43.9	0.84	0.714	6.7	HVAB
5	Soldier Creek, Book Cliff	49.2	0.82	0.658	20.7	HVAB
6	Convulsion Canyon, Salina	45.3	0.85	0.502	35.5	HVAB
7	Morby Seam, Coalville	59.0	0.84	0.527	18.1	HVCB
8	Coal Basin (Colorado)	26.0	0.71	--	--	MVB

[a] Data for Samples 1-7 from Reference 6.
Sample 8 from Reference 8.

Table 2

Hydrogenolysis Products

Sample	Conversion,[a] % coal	Heavy oil,[a] % coal	Heptane Soluble Fraction		
			% of Heavy oil	Molecular weight	H/C
1[b]	86.2	67.4	59.0	298	1.34
2	71.0	53.4	47.1	280	1.32
3	79.6	55.3	71.3	289	1.30
4	73.5	60.0	43.3	284	1.39
5	37.3	20.3	49.7	293	1.28
6	53.3	37.8	65.8	280	1.22
7	26.3	7.1	66.7	286	1.41
8	47.5	28.9	53.9	273	1.08

[a] Data from Reference 6.

[b] 3% $ZnCl_2$.

IRON CARBONYL CATALYZED REDUCTIONS OF MODEL COAL CONSTITUENTS UNDER WATER GAS SHIFT CONDITIONS

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INTRODUCTION

Liquefaction and heteroatom removal are of importance in adapting coal into fuels and chemical feedstocks which now depend on petroleum. Soluble reagents and catalysts are needed to deal with coal solids. Iron pentacarbonyl has been found to be an economically viable reagent and/or catalyst for up-grading coal; studies of its use in desulfurization and hydrogenation have been reported (1). In fundamental studies at UCLA our objective is to elucidate the reactivity of iron carbonyl under water gas shift (WGS) conditions towards organic substrates that model coal structure. Our work is paralleled by similar studies using a variety of other metal carbonyls, (2) and is preceded by studies of Wender and Orchin and their co-workers using cobalt carbonyl (3,4).

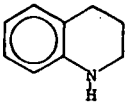
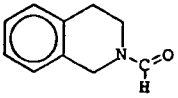
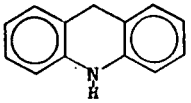
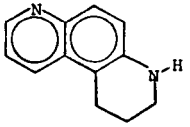
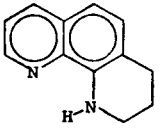
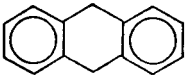
EXPERIMENTAL

Glass reaction vessels, fitted to a 0.3 L copper lined autoclave or a 0.1 L stainless steel autoclave were used for all studies. Reactions were analyzed by extracting the glass liner contents with CCl_4, drying with $MgSO_4$ and removing solvent on a rotary evaporator. Characterization was perfomed by IR, GC, ^1H and ^{13}C NMR and mass spectral methods. Gas sampling above the reaction mixture shows both H_2 and CO_2 (by gas chromatography) indicating that the water gas shift reaction had taken place. Control experiments in which no iron complex was present were performed for all reported reactions. Acridine is the only compound that is significantly hydrogenated under the control conditions; the other substrates are unaffected unless iron carbonyl is also present.

RESULTS AND DISCUSSION

Reactions in methanol, water and base under carbon monoxide pressure were initially performed at 150°C to optimize the iron carbonyl catalyzed water gas shift reaction (5,6) see Table I. Nitrogen heterocycles are readily hydrogenated under these conditions. Quinoline, 1, is 100% hydrogenated in the nitrogen-containing ring. Isoquinoline, 3, is both hydrogenated and N-formylated to 4 (7), similarly in 100% yield. Hydrogenation of only one of the two nitrogen containing rings of the phenanthrolines, is

Table I. Reductions with Iron Carbonyl Catalyzed Water Gas Shift System

Substrate	Product		Yield[a,b]
Quinoline 1		2	100%
Isoquinoline 3		4	100%
Acridine 5		6	100%
4,7-phenanthroline 7		8	75%
1,10-phenanthroline 9		10	50%
anthracene 11		12	25%

[a]Reaction conditions are as follows: 150°C, 42 $kgcm^{-2}$, 15 h in CH_3OH (75 ml) H_2O (25 ml) KOH (4.8 g), substrate (5.0 mmol) and $Fe(CO)_5$ (2.5 mmol).

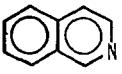
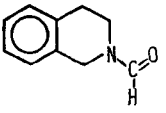
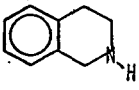
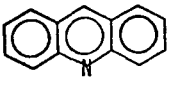
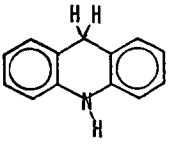
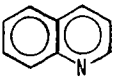
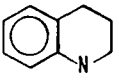
[b]Under the above conditions but without $Fe(CO)_5$, no reactions are observed.

observed. The yield of **10** is significantly reduced since it forms iron complexes as indicated by a brightly colored aqueous phase partially characterized by ^1H NMR of acetone-d_6 extracts. Anthracene is relatively unreactive under these conditions. We have however found ways in which its hydrogenation may be significantly increased, see below. Compounds which we found to be unaffected at 150 °C are naphthalene, phenanthrene, dibenzyl, anisole, diphenyl ether and dibenzthiophene.

In light of the 100% yields observed in the conversions of 1, 3 and 5 these reactions were performed using catalytic amounts of iron carbonyl; the results are listed in Table II. At 150 °C, 22 and 24 molar equivalents each of 3 and 5, respectively, are hydrogenated. At slightly higher temperatures, $Fe(CO)_5$ catalyzes the hydrogenation of 1 with an activity of 43 turnovers.

TABLE II

REDUCTIONS OF NITROGEN CONTAINING HETEROCYCLES USING CATALYTIC AMOUNTS OF $Fe(CO)_5$

SUBSTRATE	RATIO[A]	T/°C	PRODUCT AND TN[B]	
	55 : 1	150		(22)
"	55 : 1	300	"	(14)
				(21)
	28 : 1	150		(24)
	250 : 1	180		(43)

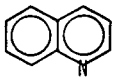
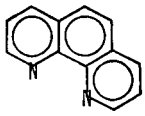
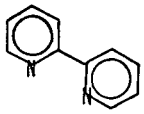
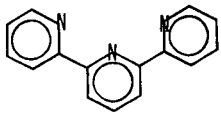
A) RATIO OF SUBSTRATE TO $Fe(CO)_5$

B) MOL OF PROD./ MOL OF $Fe(CO)_5$

Reactions were next undertaken at 300 °C to parallel coal liquefactions which are observed in higher yield at the higher temperature (8). Using catalytic amounts of $Fe(CO)_5$, isoquinoline is again N-formylated and hydrogenated with a total of 35 turnovers (Table II). Dibenzothiophene, on the other hand, remains unreactive. Other studies at 300 °C are summarized in Table III. The first entry shows that anthracene, when treated by itself is less converted (19%) than it was at 150 °C. It occurred to us that some of the constituents in coal, itself, might affect the catalytic properties of $Fe(CO)_5$. We therefore carried out experiments in which the reduction of anthracene was investigated in the presence of the substances listed in the next four entries in Table III. With these a greater degree of conversion of anthracene to 12 is observed. The

TABLE III

NITROGEN HETEROCYCLES ENHANCING THE HYDROGENATION OF ANTHRACENE TO 9,10-DIHYDROANTHRACENE, 1, AT 300°C. [A]

HETEROCYCLE	YIELD OF 1/ MOL $Fe(CO)_5$
NONE	19%
	25%
	37%
	62%
	296% (461%)[B]

A) REACTION CONDITIONS AT 300°C : CO, 70 $KGCM^{-2}$, 1 H IN H_2O (2.5 ML), KOH (2.8G), SUBSTRATE (3.0 MMOL), HETEROCYCLE (3.0 MMOL) AND $Fe(CO)_5$(3.0 MMOL).

B) CO, H_2O AND KOH AS ABOVE BUT WITH PHASE TRANSFER CATALYST ADDED: Me_4NCl (1.5 MMOL); OTHER CONSTITUENTS, $Fe(CO)_5$ (1.5 MMOL); TERPYRIDINE (1.5 MMOL); ANTHRACENE (15 MMOL).

nitrogen heterocycles are thus beneficial to reductions catalyzed by iron pentacarbonyl while quinoline and phenathroline are themselves undergoing conversion to partially hydrogenated (and/or N-formylated) products. Notably, the nitrogen heterocycles phenathroline, dipyridyl and terpyridyl which may participate as chelating ligands on iron were more effective for hydrogenation of anthracene than quinoline.

The effect on the reduction of anthracene of a phase transfer catalyst added either by itself or together with dipyridyl is summarized in Table IV. In such additions, dramatic increases are observed in the reduction. Such results at 300°C contrast the work of Alper and co-workers who at room temperature observed no benefit of a phase transfer agent in the reduction of aromatic nitro compounds by $Fe(CO)_5$ (or $Fe_2(CO)_9$) (9). The presence of tetrabutylammonium iodide increases the yield of 9,10-dihydroanthracene 44 times. Combining Bu_4NI and dipyridyl with $Fe(CO)_5$, gives the greatest reduction of anthracene, 17.1 turnovers.

The role of the phase transfer catalysts is most likely to increase the base concentration in the vicinity of the iron catalyst and further, to solubilize the anionic iron intermediates in the organic phase. The last entry in Table IV represents an experiment where the tetraalkylammonium phase transfer catalyst and the base are combined in the form of Me_4NOH. With this reagent the product yield is comparable to that originally achieved with 42 equivalents of KOH.

TABLE IV

EFFECT OF PHASE TRANSFER AGENTS AND PHASE TRANSFER AGENTS WITH DIPYRIDYL FOR ENHANCING THE HYDROGENATION OF ANTHRACENE TO 9,10-DIHYDROANTHRACENE, 1[A]

PHASE TRANSFER AGENT	TURNOVER[B]	TURNOVER W/DIPYRIDYL
NONE	0.32	0.62
Me_4NCL	1.0	3.0
$BzEt_3NCL$	-	1.3
Bu_4NI	14.2	17.1
Me_4NOH[C]	0.54	

[A] CONDITIONS AS BEFORE AT 300°C

[B] MMOL OF 1/MMOL OF $Fe(CO)_5$

[C] KOH EXCLUDED FROM THIS REACTION.

Some preliminary experiments to elucidate the principal catalyst species in solution and mechanistic features of the reductions were undertaken. To determine the principle iron carbonyl species at reaction conditions, aliquots were withdrawn from the autoclave at 175° C. IR spectra of these obtained within 3 min of sampling indicate that $HFe(CO)_4^-$ is the principal iron carbonyl species (10).

Since the principal species may not be the catalytically active species some other possible candidate complexes were tested as catalysts; these are shown in Table V. All proved inferior to $Fe(CO)_5$ even in the presence of dipyridyl. Of special significance is that cluster compounds, which are known to constitute thermal degradation products of metal carbonyls, were equally less effective as the loaded forms of the catalyst than iron pentacarbonyl.

TABLE V

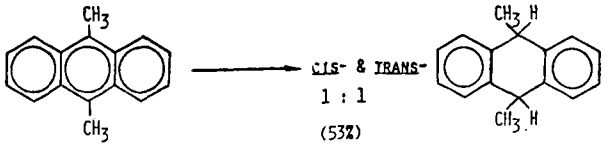
COMPARISON OF IRON(0) COMPLEXES FOR THE HYDROGENATION OF ANTHRACENE TO 9,10-DIHYDROANTHRACENE, 1[A]

COMPLEX	TURNOVER[B]	TURNOVER W/DIPYRIDYL
$Fe(CO)_5$	14.2	17.1
$Fe(COT)(CO)_3$	7.1	
$Fe_3(CO)_{12}$		3.4
$(Et_3NH)[HFe_3(CO)_{11}]$		11.2

A CONDITIONS AS BEFORE AT 300°C

B MOL EQUIV OF 1/EQUIV OF IRON(0)

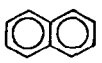
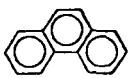
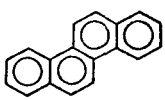
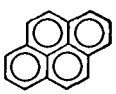
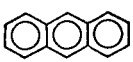
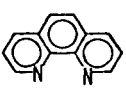
Finally, we tested dimethylanthracene to elucidate whether a cis-concerted addition or some other process were taking place in the hydrogenation (11). Our results are shown in reaction 1.



1)

We observe a 48%:52% mixture of the cis and trans isomers suggesting that either an electron transfer or hydrogen atom transfer is the initial step of reduction. The reduction potentials of a number of the compounds studied and their ability to be reduced under iron carbonyl catalyzed WGS conditions is shown in Table VI. A correlation is seen among these data, (12), supporting an electron transfer process as the initial step in the reduction of the aromatics.

TABLE VI
CORRELATION OF HYDROGENATIONS UNDER $Fe(CO)_5$ CATALYZED WGSR WITH $E_{\frac{1}{2}}$ VS SCE

SUBSTRATE		$E_{\frac{1}{2}}$/V	
	PYRIDINE	-2.52	NOT REDUCED
	NAPHTHALENE	-2.50	"
	PHENANTHRENE	-2.45	"
	CHRYSENE	-2.32	"
	PYRENE	-2.11	"
	ANTHRACENE	-1.94	REDUCED IN MIDDLE RING
	QUINOLINE	-1.14	REDUCED IN NITROGEN-CONTAINING RING
	1,10-PHENANTHROLINE	1.06	"

CONCLUSION

Iron pentacarbonyl catalyzes the hydrogenation of nitrogen heterocycles regioselectively in the nitrogen containing ring and anthracene is hydrogenated in the middle ring under water gas shift conditions above 150 °C. Chelating nitrogen heterocycles activate the $Fe(CO)_5$ toward anthracene hydrogenation. Phase transfer catalysts also have a pronounced enhancement effect on all reductions. There is thus high potential in use of iron pentacarbonyl in hydrogenations when activated by appropriate synergistic agents. Preliminary studies suggest that these reductions proceed by an initial electron transfer process from $HFe(CO)_4^-$.

ACKNOWLEDGMENT

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THE ORGANIC CHEMISTRY OF CALCIUM: A NEW PHENOL SEPARATION/RECOVERY APPROACH

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INTRODUCTION

Phenols (e.g. phenol,cresols, xylenols) comprise a significant fraction of most coal liquids. Alkylphenols alone comprise up to 20 wt% of the liquid products from such direct coal liquefaction processes as H-Coal, Solvent-Refined Coal (SRC) and the Exxon Donor Solvent (EDS) process. The toxic, corrosive and chemically reactive nature of phenols is a potential source of problems in the direct utilization of coal liquids as synthetic fuels.

One of the more common schemes for separating phenols from coal liquids involves treatment with aqueous caustic to produce water-soluble sodium phenates. After separation of the raffinate, treatment of the sodium phenate solution with an acid, such as carbon dioxide, can be used to reconstitute the phenols.(1) One major difficulty with this method is the co-extraction of non-phenolic organic materials into the aqueous phase along with the phenols. These co-extracted organics can subsequently appear as impurities in the recovered phenols, thereby rendering the phenolic stream sufficiently impure to preclude its use as a chemical feedstock for the production of polymers or polymer intermediates. This paper describes new organocalcium chemistry which allows separation and recovery of phenols from hydrocarbon streams, and which avoids the difficulties descussed above.

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere to exclude carbon dioxide and oxygen. Transfers of solids were performed in a glove box. A small positive pressure of nitrogen was maintained during half-salt preparations, using a mineral oil bubbler as a pressure relief. A Perkin-Elmer Model TGS-2 Thermogravimetric System, or a comparable unit assembled from components, was used for TGA studies. Under argon, the TGA oven was programmed from ambient to 850°C at 10°C/min, then heating was continued at 850°C under air for residue combustion. Elemental analyses were performed by personnel of the ER&E Analytical and Information Division.

Materials.

Commercially obtained solvents and reagents were of analytical reagent quality and were used as-recieved. Sodium phenate and potassium phenate were prepared from phenol and the corresponding hydroxide, as described by Kornblum and Lurie.(7)

Preparation of Calcium Half-Salt of Phenol in Aqueous Slurry.

A two-liter flask was charged with 37.0 g of calcium hydroxide (0.50 mole), 47.0 g of phenol (0.50 mole) and 1 liter of carbon dioxide-free water. The flask was fitted with a magnetic stirring bar, and a condenser which was connected to a low-pressure nitrogen source. The stirred reaction slurry was heated at 85-90°C for 16 hr, then filtered while still hot. The product was isolated by evaporating the filtrate to dryness under reduced pressure, then drying the solid to constant weight under vacuum. The yield of calcium half-salt was essentially quantitative, 74.4 g (theoretical yield: 75.1 g).

The elemental composition of the product is given in Table I.

Preparation of Calcium Half-Salt of Phenol in Benzene.

The reaction of calcium hydroxide with excess phenol in benzene is described to illustrate the general procedure used to prepare half-salts in organic media.

A 500-ml Erlenmeyer flask was charged with 9.91g of calcium hydroxide (134 mmol), 25.2 g of phenol (268 mmmol, 2-fold molar excess) and 450 ml of benzene, then attached to a low-pressure nitrogen source. The reaction slurry was stirred for 72 hr at ambient temperature then filtered, washing the filter cake thoroughly with benzene to remove unreacted phenol. The resulting solid was dried to constant weight at 50°C under vacuum to give 18.8 g of the calcium half-salt (93% of the theoretical yield, 20.1 g) as a fluffy, white powder (Found: 47.39% C, 3.97% H, 25.94% Ca, 22.13% O by NAA; Calculated: 47.98% C, 4.03% H, 26.69% Ca, 21.31% O).

The TGA of this product is shown in Figure 1. An X-ray analysis (powder pattern) indicated that no significant amount of calcium hydroxide remained. No weight was lost when a 5-g sample of the solid was extracted for 72 hr with ether in a Soxhlet apparatus, and no phenol was found by GC analysis of the ether extracts.

Pyrolysis of Calcium Half-Salt of Phenol.

The pyrolysis of the calcium half-salt of phenol at 650°C for 60 min. is described to illustrate the general procedure used for pyrolyses in the minipyrolyzer (Figure 2).

In a nirogen-flushed glove box, the quartz retort was charged with 1.55 g of the phenol half-salt (10.3 mmol) and a gas bag was attached to the condenser vent. Dry Ice was added to cool the condenser, and the retort was plunged into the preheated block which was maintained at 650°C. After 1 hr, the retort was removed from the block and the condenser was allowed to warm to room temperature. The gas bag, which contained only a small amount of gas was removed and discarded. The retort contained 0.61 g of residue (39% of the charge, theoretical amount of CaO: 0.59 g). From the condenser, 0.93 g of liquids (60% of the charge, theoretical amount of phenol: 0.97 g) was recovered using a small amount of methylene chloride solvent. Analysis by GC indicated that phenol (97%) and a trace of diphenyl ether comprised the liquid products. Thus, a 94% phenol recovery and a nearly quantitative mass balance were obtained in this experiment.

Preparation of Calcium Diphenate in Toluene.

To a one-liter, round-bottommed flask was charged 7.41 g of calcium hydroxide (100 mmol), 23.5 g of phenol (250 mmol) and 700 ml of toluene. The flask was fitted with a magnetic stirring bar and a Dean-Stark trap to which was fitted a reflux condenser connected to a low-pressure nitrogen source. The stirred reaction mixture was heated under reflux for 72 hr, then filtered. Solvent was evaporated under reduced pressure, and the resulting brown solid was dried to constant weight under vacuum at 50°C. The yield of calcium diphenate was 15.14 g (70% of the theoretical yield of 22.63 g; Found: 61.86% C, 4.48% H; Calculated: 63.70% C, 4.45% H, 17.71% Ca, 14.14% O).

RESULTS AND DISCUSSION

When analytical reagent grade phenol was treated with an equimolar amount of calcium hydroxide in a water slurry at 85-90°C, a salt was formed which was not calcium diphenate, PhO-Ca-OPh, as shown in Table I. Instead, the data are consistent with formation of the calcium half-salt, PhO-Ca-OH (Eq. 1). This compound had previously been prepared by treating calcium diphenate with a mixture of carbon monoxide and hydrogen at 105 - 110°C.(2)

$$Ph\text{-}OH + Ca(OH)_2 \xrightarrow{25 - 100°C} Ph\text{-}O\text{-}Ca\text{-}OH + H_2O \qquad (1)$$

Calcium half-salts can also be prepared in organic media. The products obtained by reacting a two-fold excess of phenol with calcium hydroxide in benzene, toluene, xylene, pentane or cyclohexane slurries at 25°C were identical to those of the half-salt obtained in water. Thus, formation of calcium half-salts is a general reaction, and is not specific to the aqueous medium.

Under the mild conditions discused above, the calcium phenol half-salt is not sufficiently basic to react with additional phenol to form calcium diphenate. In a toluene slurry, calcium diphenate could, however, be obtained under forcing conditions: 72 hr under reflux with continuous separation of water (Dean-Stark trap).(3) The product was isolated by evaporating to dryness under reduced pressure. Calcium diphenate so produced was readily soluble in a variety of organic solvents including benzene, toluene, xylene and ether. In contrast, the calcium half-salt of phenol was insoluble in these solvents, and in dipolar aprotic solvents, such as tetrahydrofuran, N,N-dimethylformamide and N-methylpyrrolidone. Further support for the proposed half-salt structure was obtained from X-ray diffraction (powder pattern) experiments, which indicated the absence of calcium hydroxide in the product. Extraction of the product salt with ether in a Soxhlet apparatus failed to remove phenol, thereby ruling out the possibility of physically adsorbed phenol and confirming the half-salt structure.

The thermal chemistry of the calcium half-salt of phenol is most interesting. When the material was heated at a programmmed rate of 10°C/min in a thermogravimetric analyzer (TGA) under argon, it was stable to about 450°C (Figure 1).(1) Upon continued heating, devolatilization of the sample occurred (450-650°C) with a weight loss corresponding to the loss of phenol. An X-ray diffraction analysis of the 650°C residue revealed that calcium oxide and some calcium hydroxide were present. Further heating to 850°C in the presence of air led to a very small additional weight loss and to a residue which X-ray analysis showed to be essentially pure calcium oxide. Both at 550°C and 650°C in a small, batch pyrolysis apparatus (minipyrolyzer, Figure 2) the calcium half-salt of phenol yields phenol as the major volatile organic product (Equation 2). Table II summarizes the pyrolysis data.

$$\text{Ph-O-Ca-OH} \xrightarrow{\text{Pyrolysis at 550-650°C}} \text{Ph-OH} + \text{CaO} \qquad (2)$$

In a similar manner, the calcium half-salt of p-cresol was prepared. Thermal stability of the p-cresol half-salt is comparable to that of the phenol half-salt, but the presence of the side chain alters the distribution of products on pyrolysis, as shown in Table III. At the lower pyrolysis temperature of 550°C, cresols are the only significant products, though conversion is slow. At 650°C however, thermal cracking reactions become important. In this case, both hydrogen and methane were found in the gas product. Phenol, presumably produced by thermal dealkylation, was found in the liquids, along with the cresols.

These results are in sharp contrast to the pyrolyses of sodium phenate and potassium phenate, which under comparable conditions yield a char and gas, but essentially no volatile liquid organic products.(2,4)

The unexpected results with the organocalcium system suggested a new phenol separation and recovery approach based on the reactions shown in Equations 1 and 2. We have demonstrated phenol recovery via this half-salt technique, using both model compounds and raw naphtha from the EDS coal liquefaction process.(5,6)

CONCLUSIONS

The reaction of calcium hydroxide with phenols in aqueous or organic media provides a simple method for preparing the corresponding calcium phenol half-salts. In sharp contrast to pyrolyses of alkali metal phenates which yield gas and char, pyrolyses of calcium phenol half-salts yield calcium oxide and phenols. The unexpected results with the organocalcium system suggested a new phenol separation/recovery approach.

ACKNOWLEDGEMENTS

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Table I. Elemental composition of the salt obtained from calcium hydroxide and phenol in an aqueous slurry at 85-90°C.

Element	$Ca(OPh)_2$ Calculated, Wt%	PhO-Ca-OH Calculated, Wt%	Calcium Salt Found, Wt%
Carbon	63.7	48.0	46.0 (±0.4)
Hydrogen	4.4	4.0	3.89 (±0.04)
Calcium	17.7	26.7	26.8 (±0.4)

Table II. Pyrolysis of the calcium half-salt of phenol in the minipyrolyzer gives phenol and calcium oxide.

Temperature, °C	Residence Time, minutes	Product Yields, Wt% Solid	Liquid	Liquid Yield, % of Theoretical	Liquid Analysis, Wt% Ph-OH	Ph-O-Ph
550	5	77 (±1)	24 (±2)	38	97 (±2)	Trace
650	5	60 (±2)	39 (±2)	62	94 (±1)	2
650	60	40 (±2)	60 (±2)	96	97 (±1)	Trace

Table III. The side chain alters product distribution in the pyrolysis of the p-cresol half-salt.

Temperature, °C	Residence Time, minutes	Product Distribution, Wt% Solid	Gas	Liquid	Liquid Yield, % of Theoretical	Liquid Analysis, Wt% Phenol	Cresols
550	5	92	---	8	12	--	98
650	5	61 (±1)	4 (±3)[a]	35 (±3)	59	24 (±1)	38 (±3)

(a) Approximately 80 wt% methane and 16 wt% hydrogen by mass spectrometric analysis.

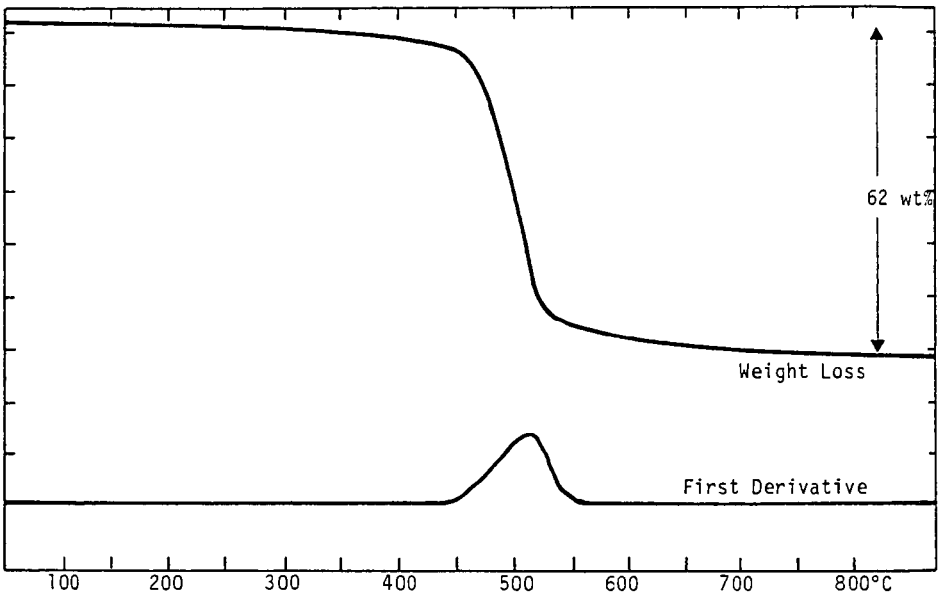

Figure 1. The weight lost during TGA of the calcium half-salt of phenol corresponds to loss of phenol.

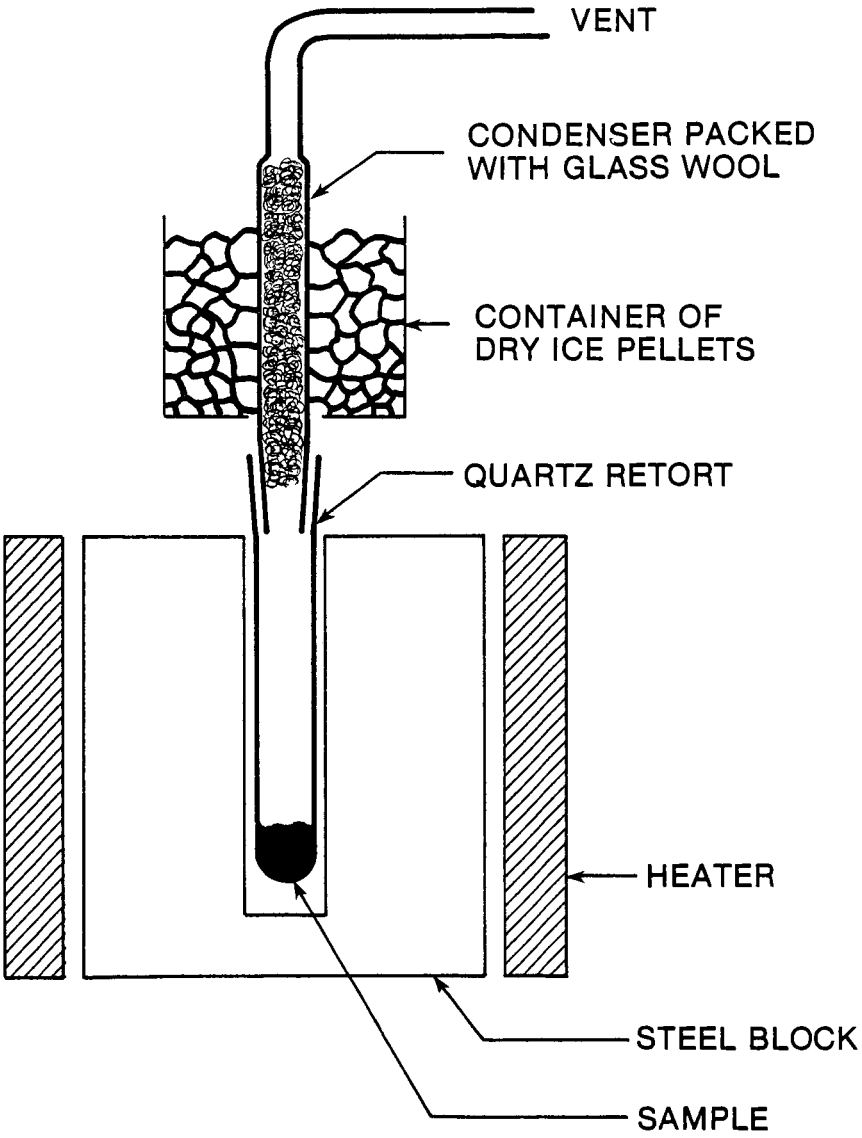

FIGURE 2. MINIPYROLYZER

Rapid Determination of Bitumen, Varsol and Other Solvents Using Proton N.M.R.

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Introduction

The extensive Athabasca oil sands are assuming an increasing role in supplying Canada's liquid hydrocarbon needs. One commercial plant, Suncor Inc., has operated since 1967. It extracts bitumen from the oil sands and subsequently upgrades to synthetic crude oil. Syncrude Canada Ltd. which is designed to produce 109,000 barrels of synthetic crude per day, began production in 1978. Fundamental to the successful utilization of this oil sand resource and to the economic operation of the extraction plant is a reliable analytical method for the analysis of bitumen rich froth collected from the hot water extraction process. This froth must be further treated to remove solid particles and water. The purification process consists of a diluent addition step to lighten the hydrocarbon density, two centrifuging stages to remove solids and water, and a diluent recovery step. Analytical inspection of these process streams includes analysis for bitumen, diluent, water and solids. The analyses are needed for process control and material balance calculations.

The current determination of bitumen, diluent, water and solids is performed by separating the sample into the individual components. The solvent/hydrocarbon solution must be further analyzed for diluent (naphtha) and bitumen content. Bitumen is usually determined spectrophotometrically while diluent (naphtha) is either determined by difference or by G.C. (2). The most common problems with these methods are the greater sources of errors involved (2). If the naphtha is determined by difference all the errors will accumulate in the results for this component. In the G.C. method errors will arise from dilution and the small volume required for injection (1 µl) (2). Also the adsorption of asphaltenes from bitumen on the column packaging materials limits the use of G.C. for the estimation of the diluent in the presence of bitumen.

In this paper we report the proton nmr results for the quantitative estimation of bitumen and a diluent (naphtha or varsol) in the presence of toluene, benzene or methylene chloride, three commonly used solvents for the extraction of bitumen from oil sands.

Experimental Methods

a) Proton nmr measurements were performed on a Varian EM-360 nmr spectrometer (60 MHz); 500 µl of solution was used in each case in a 5 mm internal diameter tube. Carbon tetrachloride or tetrachloroethylene was used as solvent. Gain and amplitude were adjusted to give integrations within the range of the chart paper using lowest and highest concentrations. Once adjusted all the parameters were kept constant for subsequent measurements. Integration limits for the aromatic region of benzene, CH_2-group of methylene chloride and

the CH_3-group of toluene are well defined and can be easily measured. However, it is difficult to decide the starting point for the integration for the methyl region of bitumen, varsol or naphtha at ca. 1.0 ppm downfield from tetramethylsilane. This is because of the overlap of the methylene and methyl regions. It was therefore decided to take the mid point of the two peaks (methyl and methylene) as the start for the integration. The integration limits for methyl regions were therefore as illustrated in fig. 8a. Proton nmr spectra for bitumen, varsol, bitumen + varsol, toluene, benzene, methylene chloride, bitumen + varsol + toluene and bitumen + varsol + benzene are shown in figures 6-8 to illustrate the portions integrated for calibration curves.

b) Preparation of Standard Bitumen Solution: Bitumen was extracted from a sample of high grade oil sand using toluene in a Soxhlet apparatus (2). Non-filtered solids were removed from the bitumen solution by passage through a 0.45 μm millipore filter paper. The solvent was removed in a Brinkmann rotary evaporator at 100°C under reduced pressure. The total time required to remove the solvent from a 100 gram sample was less than one hour. The residual solvent was then measured using infrared spectroscopy (3) and proton nmr.

c) Calibration Curves: (1) Bitumen: - A standard sample of the bitumen required for the calibration curve was prepared as outlined above. The amount of the residual toluene quantitatively determined by infrared and proton nmr, was applied as a correction to the bitumen content. A stock solution (35.0% w/v) of bitumen in carbon tetrachloride and another in tetrachloroethylene were prepared from the standard bitumen accurately weighed to the nearest 0.0001 gram. Serial dilutions of bitumen, ranging in concentration from 3-35%, were prepared and the areas of the methyl peaks were determined from the integration of the peaks at ca. 1.0 ppm downfield from tetramethylsilane in the proton nmr spectrum. A plot of the per cent bitumen vs area of the methyl peak produced a straight line passing through the origin, with a slope of 0.51.

$$\% \text{ Bitumen} = \frac{\text{Area of the methyl peak}}{0.51}$$

(2) Diluent: Measurements were made for two bitumen diluents, namely naphtha and Varsol (Stoddard solvent). Solutions of both naphtha and Varsol ranging in concentrations from 3-60% w/v were prepared. Areas of the methyl peaks at ca. 1.0 ppm downfield from tetramethylsilane were determined as described above for bitumen. The plots of the per cent naphtha and Varsol vs area of the methyl peak produced straight lines passing through the origin. Slopes for the two plots were 1.17 and 0.95 for % w/v concentrations and 0.85 and 0.75 respectively for % v/v concentrations. The concentration of the diluent was determined as follows:

$$\% \text{ Diluent} = \frac{\text{Area of methyl peak}}{\text{Slope}}$$

(3) Toluene, Benzene and Methylene Chloride: Carbon tetrachloride solutions of toluene, benzene and methylene chloride were prepared ranging in concentrations from 1-20% (10% in the case of benzene). Areas of the methyl peak for toluene, CH_2-peak for methylene chloride and aromatic peak of benzene were measured from their proton nmr spectra. Plots of per cent concentration vs areas were straight lines in each case. The concentrations were calculated using the following equations.

$$\% \text{ (v/v) of Toluene} = \frac{\text{Area of the methyl peak}}{5.64}$$

$$\% \text{ (v/v) of Benzene} = \frac{\text{Area of the peak from proton nmr}}{13.75}$$

$$\% \text{ (v/v) of Methylene Chloride} = \frac{\text{Area of } -CH_2 \text{ peak}}{5.64}$$

(d) Determination of Varsol/Bitumen in a mixture.

Area of the methyl peak, measured as outlined in 1 or 2 above, represents the total area due to contributions from both diluent and bitumen. Bitumen concentration was separately determined photometrically by measurements of absorption at 530 nm. Knowing the concentration of bitumen the area of the methyl peaks due to bitumen can be determined from the equation in 1 above.

Area of the methyl peaks in bitumen = 0.51 × % (w/v) Bitumen

Concentration of the diluent can then be calculated as follows:

$$\frac{\text{Total Area of the methyl peak - Area due to bitumen } CH_3 \text{ group}}{\text{slope}}$$

Results and Discussion

The calibration curves for benzene, toluene, methylene chloride, bitumen and diluents (Suncor naphtha and Varsol) are shown in figures 1, 2 and 3. All plots are good straight lines with zero intercepts. This is indicative of the existence of a linear correlation between the per cent concentrations and the area of the proton nmr signals emphasising the usefulness of proton nmr in the quantitative estimation of concentrations.

The measurements involving bitumen and diluent were performed independently in two solvents, carbon tetrachloride and tetrachloroethylene. Results were found to be independent of the solvent indicating no loss due to evaporation of the carbon tetrachloride during the period of measurement. Benzene, toluene and methylene chloride were only studied in carbon tetrachloride.

Procurement of unaltered standard samples of bitumen from oil sands is a serious problem recognised by Clark in 1950 (1). Oil does not separate from the native sands and water without the use of either chemical agents, solvent, heat or extreme mechanical force, all of which may significantly alter the oil. Since no method of separation exists that can guarantee an oil sample free from alteration, the first problem encountered in obtaining a standard sample of bitumen is the development of an acceptable separation procedure. Of the various separation methods, solvent extraction of bitumen from oil sands has been recommended as the most suitable method for this purpose (3).

The major drawback of solvent extraction methods is the fact that it is not practical to completely remove all residual solvent from the bitumen. Hence analytical techniques are required to determine the residual solvent concentration. Again proton nmr is found to be very useful for determining commonly used protonated solvents such as toluene, benzene and methylene chlorides.

Concentrations of toluene, benzene and methylene chloride determined from proton nmr compare reasonably well with the actual

values. Accuracy of the nmr method is evident from the values of the standard deviations of ± 0.116, ± 0.177 and ± 0.318 respectively. A plot of Actual vs Found concentrations is shown in fig. 4. In the case of benzene or toluene the zero intercept and slope of 1 are indicative of good accuracy. In the case of methylene chloride significant errors are introduced because of the high volatility of this solvent (b.p. 39.8°C) which makes it difficult to prepare standard solutions because of evaporative losses. Hence a much higher relative standard deviation of ±1.033 with respect to least squares plots of data at different concentrations. To remedy the problem of evaporation of the solvents from the nmr tubes we find it helpful to use teflon stoppers rather than regular plastic caps. Besides reducing evaporation the teflon caps are more resistant to solvent attack, particularly by the chlorinated solvents.

Rapid and reliable determination of diluent (Varsol/Naphtha) in bitumen/diluent mixtures is essential for process control and material balance calculations both in hot water process and solvent extraction spherical agglomeration process for the extraction of bitumen from oil sands. The traditional methods for the determination of diluent do not give the required degree of accuracy. The concentrations of Varsol as determined from proton nmr measurements are shown in fig. 5 as a plot of the actual concentrations against calculated concentrations. Zero intercept and a slope of 1 indicates a very good linear co-relation. A standard deviation of ±0.281 (wt.%) was calculated for these results. This again demonstrates the accuracy of the nmr method. Advantages of the nmr method include higher precision, shorter analysis time (actual analysis time ca. 2 minutes), broader range of applicable concentrations (0.2-70%) and small quantity of the non-consumable sample needed for analysis (500 µl).

Bitumen and diluent can be determined separately by proton nmr, in all the common solvents, e.g. benzene, toluene, methylene chloride, carbon tetrachloride and other non-protonated solvents. The results are at least as accurate as obtained by other methods.

One of the peaks of the diluent spectrum overlaps with the methyl peak for toluene. Also, there is an overlap between the aromatic region of the benzene and diluent. Hence, an accurate determination of the concentrations of benzene or toluene in presence of diluent is not possible using this method. However, the presence of toluene or benzene does not effect the determinations of the concentrations of bitumen or diluent.

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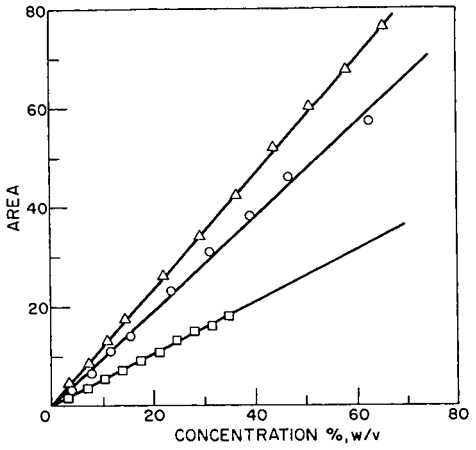

Fig. 1. Calibration Curves. Concentrations ($\frac{v}{v}$%) vs area of the ^1H nmr peaks. Benzene ○ ; Toluene □ ; methylene chloride △.

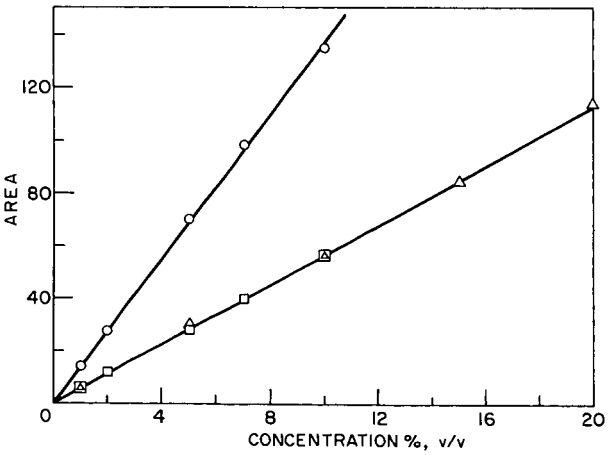

Fig. 2. Calibration Curves. Concentrations ($\frac{w}{v}$%) vs area of the methyl proton nmr peaks. Bitumen □ ; Stoddard solvent ○ ; Suncor Naphtha △ .

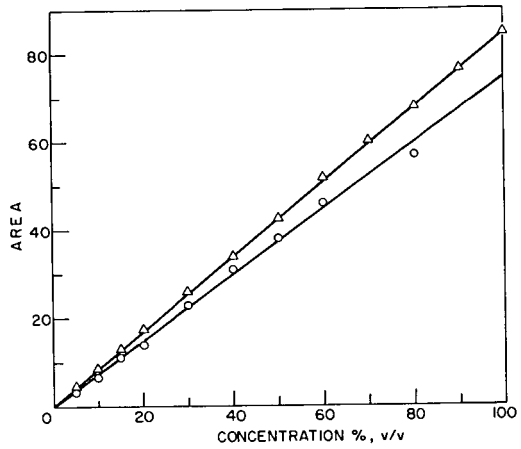

Fig. 3. Calibration Curves. Concentration ($\frac{v}{v}$%) vs area of the methyl proton nmr peaks. Varsol ○; Suncor Naphtha △.

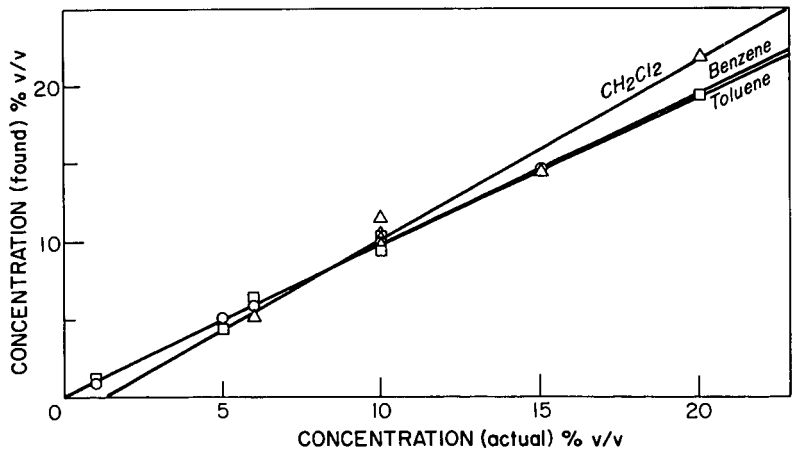

Fig. 4. Plot of the concentrations ($\frac{v}{v}$%), Actual vs Found. Benzene ○; Toluene □; methylene chloride △.

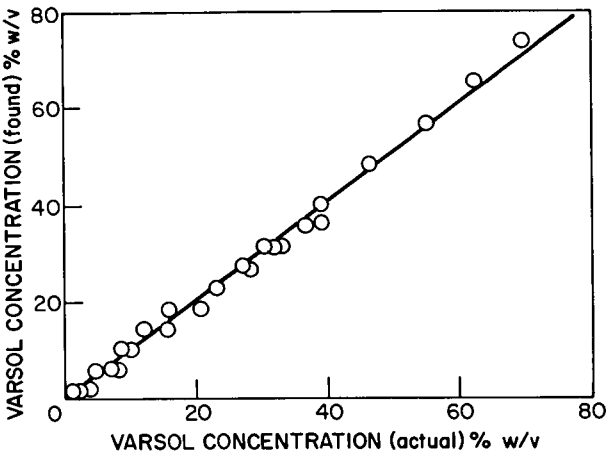

Fig. 5. Plot of the Varsol concentration actual vs Varsol concentration found.

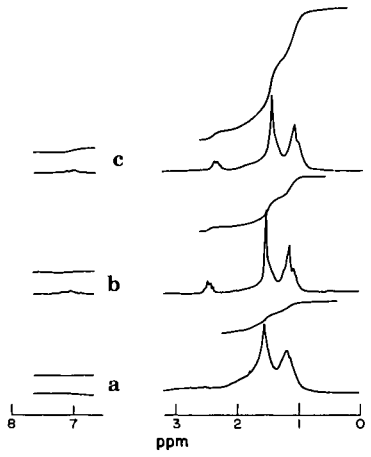

Fig. 6. ^{1}H n.m.r. spectra of a) Bitumen b) Stoddard solvent c) Bitumen + Stoddard solvent.

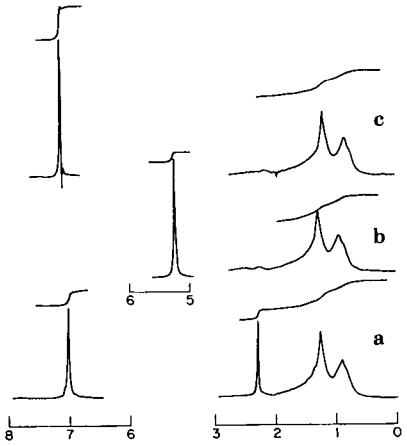

Fig. 7. ^{1}H n.m.r. spectra of a) Bitumen + Toluene b) Bitumen + methylene chloride c) Bitumen + Benzene.

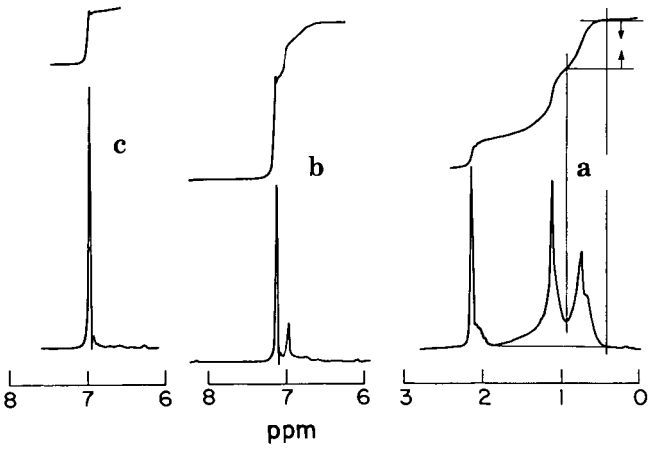

Fig. 8. ^{1}H n.m.r. spectra of a) Bitumen + Toluene + Stoddard solvent b,c) Bitumen + Benzene + Stoddard solvent.

Storage Stability Studies of Fuels Derived from Shale and Petroleum

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INTRODUCTION

In considering shale oil as an alternative and complement to petroleum as a feedstock for production of liquid fuels, important compositional differences in the heteroatom components must be taken into account. Some heteroatomic compounds, containing N, S, or O, influence both the thermal stability and storage stability of the liquid fuels. Thermal stability is the resistance of a fuel to formation of deposits on surfaces within the fuel system of an operating vehicle, and storage stability is the resistance of a fuel to formation of gums (both soluble gums and insoluble sediments) under fuel storage conditions. Thermal deposits can foul fuel/lubricating heat exchangers causing decreased efficiency and storage deposits can plug filters.

The purpose of this research is to find mechanisms of storage deposit formation in jet and diesel fuels and to characterize the deposits. Insoluble sediments are the undesirable materials for these fuels since they are injected into engines as liquids. The rate of sediment formation can be determined by traditional quantitative gravimetric procedure, usually at temperatures of 43°C or higher. These procedures require storage times of weeks or months, depending on stress temperature, to develop amounts of sediments which can be measured reliably. However, fuel storage degradation can be monitored in the early stages by laser light scattering of developing particles at ambient temperature. By carrying out extensive light scattering experiments, in the presence of certain heteroatomic compounds, we hope to find out quickly which of these compounds are deleterious to fuel stability. Stability information of this kind is useful in that refining process conditions can then be selected which will minimize fuel degradation through removal of the deleterious compounds. Ultimately, it will be important to know the trade-offs betwen processes of varying severity for removing these compounds and modifying the fuel stability.

EXPERIMENTAL

Laser light scattering measurements were carried out with a photometer described by Berry (1) modified by introduction of a laser light source. Small light-scattering cells of the design by Dandliker and Kraut (2) were used. The Pyrex cells were in the form of truncated cones, in order to reduce the stray light pickup by the detector. In order to study the effects of substituted quinolines, pyridines and indoles on deposit formation, we

adapted the method of Dahlin et al. (3) of obtaining the amount of "deposited gum" from the weight gain of a glass cover slip (22 x 40 mm) placed in a 150-ml Pyrex beaker (bottom surface area 21.61 cm^2) containing 50 ml of liquid fuel.

Degradation products obtained by heat stressing (80-120°C) fuels enriched with specific heteroatomic compounds (500 ppm nitrogen concentration) were analyzed by nuclear magnetic resonance technique. For deposits which are soluble in $CDCl_3$, both 90 MHz and 600-MHz spectrometers were used. The latter instrument operates at magnetic field of 140.9 kgauss, the highest magnetic field possible today, and has been used by Hara et al. (4) to study the very complex coal-derived liquids. For deposits which are insoluble in $CDCl_3$, magic-angle spinning, solid-state carbon-13 NMR spectra were obtained on a Varian XL-200 superconducting spectrometer at 50.3 MHz. Cross polarization of the carbon nuclei was done under Hartman-Hahn matching conditions. The sample was packed into a bullet rotor and spun at approximately 2500 Hz, and sidebands were suppressed using the Dixon Sideband Suppression technique.

RESULTS AND DISCUSSION

(A) Laser Light Scattering and Deposit Formation in Liquid Fuels

Storage techniques for determining the stability of liquid fuels require weeks or months of storage, even at elevated temperatures. A technique which has greater sensitivity for initial deposit formation could shorten the storage time and/or reduce the stress temperature. We have examined one such technique, light-scattering. As a fuel ages, particles grow in size and scatter light. Figure 1 is a plot of scattering intensity at 90° scattering angle as a function of storage time at room temperature for shale II-derived JP-5 (jet fuel, sample J22) containing various concentrations of 2,5-dimethylpyrrole (DMP), while Figure 2 is a corresponding plot for petroleum-derived JP-5 (jet fuel, sample 80-8). The data indicate that in the absence of DMP, which is especially deleterious to fuel stability, the liquid fuel is stable and little light-scattering occurs. As the concentration of DMP increases, the extent of light-scattering increases, in accordance with the increase in tendency to form deposit. The use of light-scattering technique as a monitor of aging has the advantages that room temperature is adequate and that a much shorter time of experimentation is required. The small particles which are formed on aging are believed to be precursors of sediments. Comparison of Figures 1 and 2 shows that the stability of the petroleum-derived JP-5 is less than the shale-derived JP-5.

Figure 3 is a plot of scattering intensity at different angles vs. time at room temperature for petroleum JP-5. For the bottom line, where no DMP is added, the intensity remains small and constant, and independent of the measuring angle. The uper lines are for different angles for petroleum JP-5 with 105 ppm N, DMP. The data show that scattering at 45° is much greater than at 90° or 135°. As the particles get larger, they tend to scatter light more intensely in a forward direction, resulting in a larger value of I_{45}/I_{135}.

Of all the heteroatomic compounds tested, DMP is easily the most powerful promotor of deposit formation in both petroleum- and shale-derived jet fuels. Among some other nitrogen-containing compounds tested, the

deleterious effect on shale jet fuel stability, as measured by the amount of "deposited gum" (3) formed, decreases in the order: 2,6-dimethylquinoline, substituted pyridines (2-ethylpyridine, 2,4,6-trimethylpyridine, 2,6-dimethylpyridine, 2-methylpyridine), 7-methylindole. The following compounds do not form deposited gum in the shale-derived jet fuel even when stressed at 80°C for 8 weeks: 2-methylindole, 2,5-dimethylindole, and 1,2,3,4-tetrahydroquinoline. The DMP sediment is insoluble in the usual organic solvents. The gums obtained from use of other dopants are soluble in $CDCl_3$, and therefore have been studied by solution NMR and infrared techniques.

(B) Liquid State NMR

The JP-5 fuels from shale II and petroleum have essentially identical proton and carbon-13 NMR spectra. The aromaticity is 0.10 and a considerable amount of long unbranched alkyl groups is present in both. Figure 4 gives the 600-MHz PMR spectra of shale-derived JP-5 and 2,6-dimethylquinoline (DMQ), 500 ppm N, 25 days, 80°C: top spectrum, the stressed liquid phase in $CDCl_3$; bottom spectrum, the sediment dissolved in $CDCl_3$. Many NMR signals appear in the lower field regions of the aliphatic and aromatic ranges. These indicate the polycyclic nature of the sediment, 3-4 aromatic rings. Elemental analysis of the gum gives the formula: $C_6H_7O_{1.3}$. The nitrogen content is only 1%. Thus, DMQ (which has 8.9% N) does not dominate the composition of the deposit.

(C) Solid State NMR

Magic angle spinning, carbon-13 spectra of the DMP sediments formed in shale JP-5 and in shale-derived diesel, show that oxygen is incorporated in the deposit in the form of carboxylate, carbonyl and ether linkages. For both fuels, the DMP deposits have the same formula: $C_6H_7NO_{1.5}$. Since DMP is C_6H_9N, we conclude that, unlike DMQ, DMP dominates the composition of the deposits obtained in the shale derived jet and diesel fuels. The nitrogen and oxygen contents of the sediments are 11.6 and 20.1 wt.%, respectively. These values are almost twice the corresponding values of the petroleum jet fuel-DMP sediment which has the formula $C_{17}H_{28}NO_{1.5}$: N,5.1; O,8.4%.

(D) ESCA and Fourier Transform Infrared Spectroscopy

ESCA and FT-IR techniques have been used in the study of deposits formed in shale-derived jet fuel, shale-derived diesel fuel, petroleum jet fuel, and coal liquefaction products which have been subjected to severe hydrotreatment (upgraded H-coal and SRC-II liquids). The results confirm the finding that oxygen is required in formation of deposits and that oxygen is incorporated in more than one species. We are also using these techniques to study the structure of the sulfur and oxygen species of the deposit formed in the jet and diesel fuels, in the presence of DMP and thiophenol, for the purpose of studying synergism.

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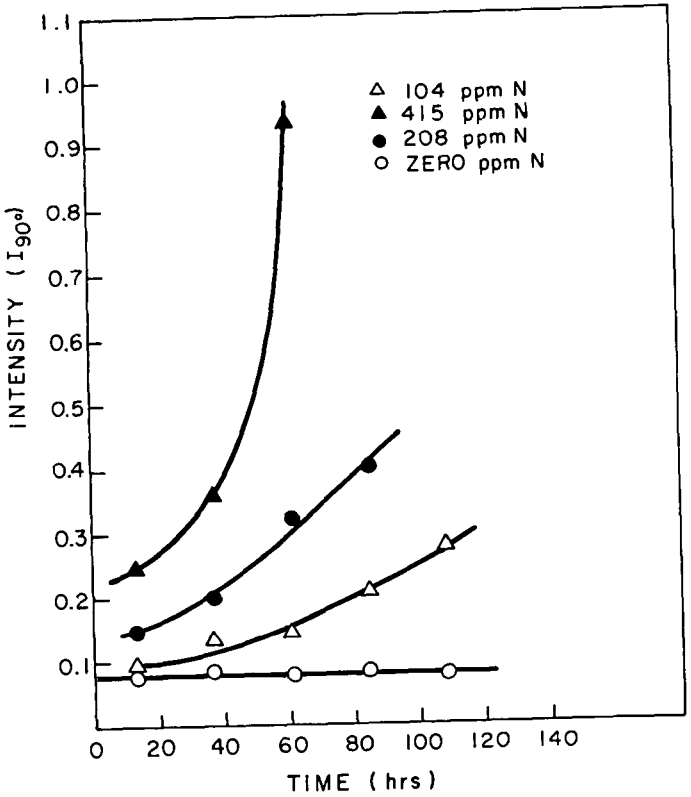

FIGURE 1. SCATTERING INTENSITY, 60°, FOR SHALE II JP-5 + DIFFERENT CONCS. DMP (ppm N) STORED AT ROOM TEMPERATURE.

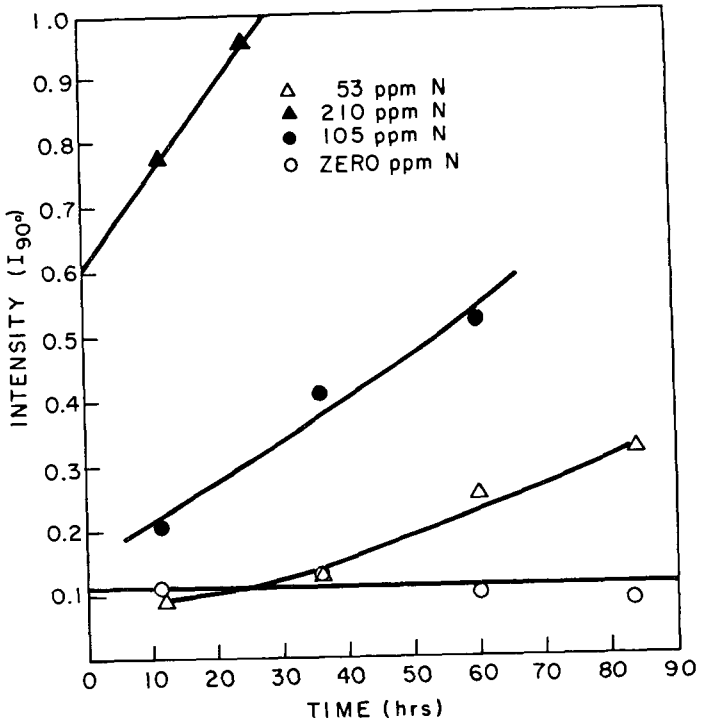

FIGURE 2. SCATTERING INTENSITY, 90°, FOR PETROLEUM JP-5 + DIFFERENT CONCS. DMP (ppm N) STORED AT ROOM TEMPERATURE.

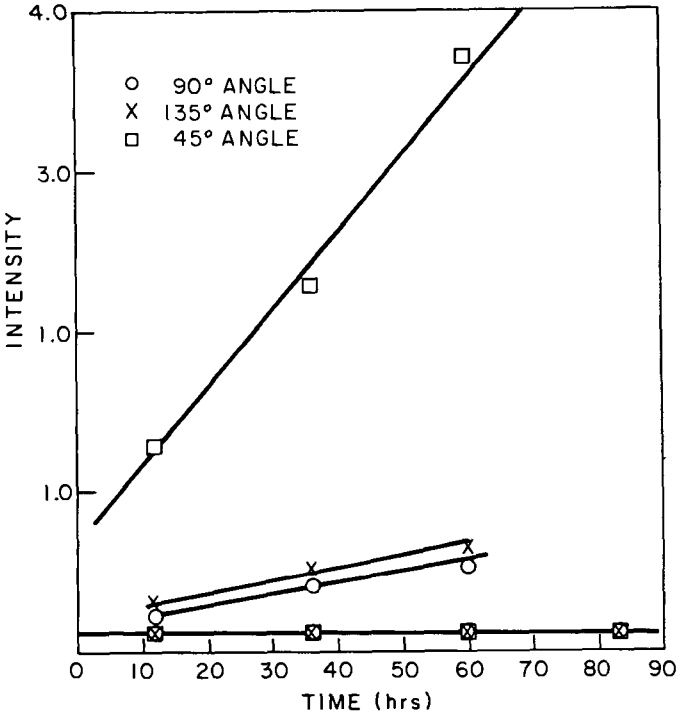

FIGURE 3. SCATTERING INTENSITY AT DIFFERENT ANGLES FOR PETROLEUM JP-5 AT ROOM TEMPERATURE. BOTTOM LINE, NO DMP; UPPER LINES, 105 ppm (N).

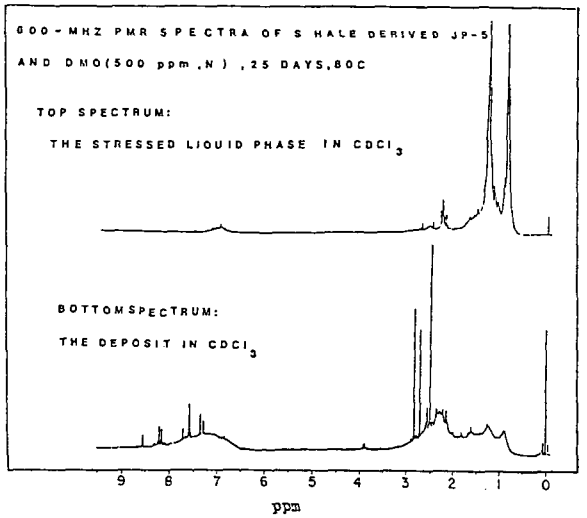

FIGURE 4.